Glass and Ceramics, Vol. 70, Nos. 5 – 6, September, 2013 (Russian Original, Nos. 5 – 6, May – June, 2013)

UDC 666.113:289’87’28

EFFECT OF THE INITIAL BATCH COMPOSITION AND HEAT-TREATMENT CONDITIONS ON THE SPECTRAL CHARACTERISTICS OF GLASSES AND GLASS CERAMIC MATERIALS IN THE SYSTEM Bi_2O_3–SiO_2–GeO_2

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Translated from *Steklo i Keramika*, No. 6, pp. 11 – 15, June, 2013.

Glasses with the compositions $Bi_4(Si_xGe_{1-x})_3O_{12}$ (x = 0.33, 0.5, 0.66 and 1.00) and glass ceramic materials based on them were obtained. The effect of the batch composition and heat-treatment regimes on the spectral characteristics of these materials was determined.

Key words: bismuth-containing glasses, glass ceramic materials, absorption spectrum.

One of the main requirements for scintillation materials is no light absorption at the wavelength of the emitted light. On excitation by high-energy UV and γ radiation colorless single crystals of silicon- and germanium eulytites ($Bi_4X_3O_{12}$, X = Ge, Si), which are needed in high-energy physics for the active elements of scintillation detectors, manifest luminescence peaking at wavelength 480 nm. Glasses and especially transparent glass ceramic materials with the same compositions with a high volume fraction of eulytite nanocrystals will be able to compete successfully with single crystals provided that their luminescence characteristics are comparable. However, the presence of a wide absorption band in the range 450 – 500 nm in the absorption spectra of the materials indicated, which results in the appearance of intense red-brown color, decreases their scintillation characteristics many-fold.

This is why the problem of decreasing the absorption coefficient of the materials in the wavelength range indicated to zero remains just as important even though the problem of obtaining high-quality initial glasses and a transparent nano-glass ceramic based on them with the required content of the crystalline phase of eulytite has been solved.

All authors explain the absorption peak in the region 450 – 500 nm by the presence of bismuth centers but there is disagreement concerning their nature (the ions Bi^+, Bi^{2+} and Bi^{5+} and dimers Bi_2, Bi_2^- and Bi_2^{2-}) [1, 2]. According to the data in [2], the authors believe that the absorption peak of these materials in the region 450 – 500 nm is due to a transition of the Bi^{3+} ions to a higher degree of oxidation (4+, 5+) as a result of prolonged melting of the glasses at 1100°C in air. Since for bismuth the degree of oxidation 3+ is most stable at temperatures below 820°C, prolonged heat-treatment (to 40 h) at 460 – 500°C makes it possible to eliminate the absorption band that prevents using the materials in scintillation detectors.

If the assertion made in [2] is correct, then to obtain directly bismuth-containing glasses and glass ceramic materials (GCM) which do not absorb in the range 450 – 500 nm the process must be conducted in a reducing atmosphere.

The aim of the present work was to study the reasons for the appearance of an absorption band in the range 450 – 500 nm and the effect of certain process parameters for obtaining spectral properties on them for glasses and GCM in the system Bi_2O_3–SiO_2–GeO_2.

These studies were directed toward the following:

1) changing the oxygen environment of bismuth in glasses absorbing in the region 450 – 500 nm by passing an electric current;

2) changing the degree of oxidation of bismuth during glass melting by adding a reducing component (oxygen content 0 – 5%[3]) to the initial batch.

Glasses with the composition $Bi_4(Si_xGe_{1-x})_3O_{12}$ (x = 0.33, 0.5, 0.66 and 1.00) were obtained by melting batch in platinum crucibles at 1100°C in a resistance furnace without forced mixing of the melt. Glass was poured onto a steel substrate pre-cooled to 18°C. To optimize the glass melting regime the experiments were performed with different melting times of the initial batch (30 min, 2 h).

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[3] Here and below the content by weight, %.

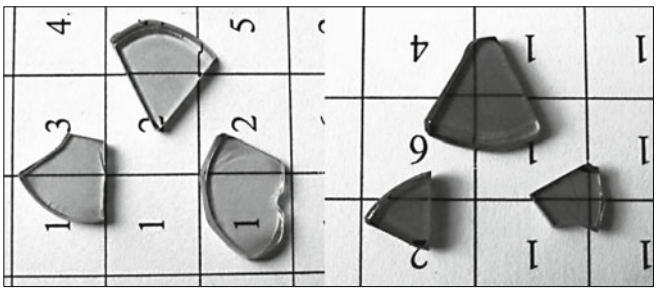

Fig. 1. Samples of $Bi_4(Si_xGe_{1-x})_3O_{12}$ (x = 0.33, 1 and 0.66) before (right-hand side) and after (left-hand side) passage of dc current during heating.

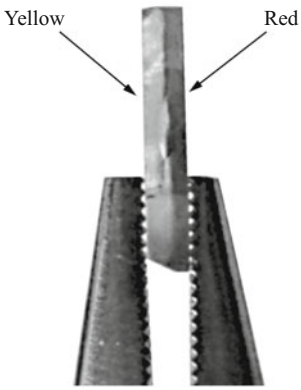

Fig. 2. Oriented distribution of the color in a sample of glass with the composition $Bi_4(Si_{0.66}Ge_{0.33})_3O_{12}$.

After passing 34.4 V dc current through the glass samples an appreciable change in glass color is observed on heating to 500°C and at the same time the sample is divided into two regions separated by a sharp boundary, the larger region being practically colorless and the smaller one dark-orange (Figs. 1 and 2). A so-called amorphous halo with no distinct peaks, which is characteristic for glass, is present in the x-ray diffraction patterns of the samples obtained.

The process of making glass with the composition $Bi_4Si_3O_{12}$ and 0.5% carbon added to the initial batch yields glass which is transparent overall with a dark tint and visible inclusions of metallic bismuth. For lower carbon content 0.05 and 0.1% the glass color becomes lighter compared with a sample with the composition $Bi_4Si_3O_{12}$ and no reducing component. The intensity of the glass color decreases with increasing carbon content, and for 0.5% carbon the color is distributed nonuniformly.

To obtain GCM samples of glass with the composition $Bi_4Si_3O_{12}$, obtained by adding a reducing component in different amounts, were heat-treated for 12 and 24 h in a muffle furnace at 420, 460 and 500°C. Glass ceramic samples heat-treated at 460°C for 25 h show different absorption intensity in the entire visible wavelength range. The transparent and

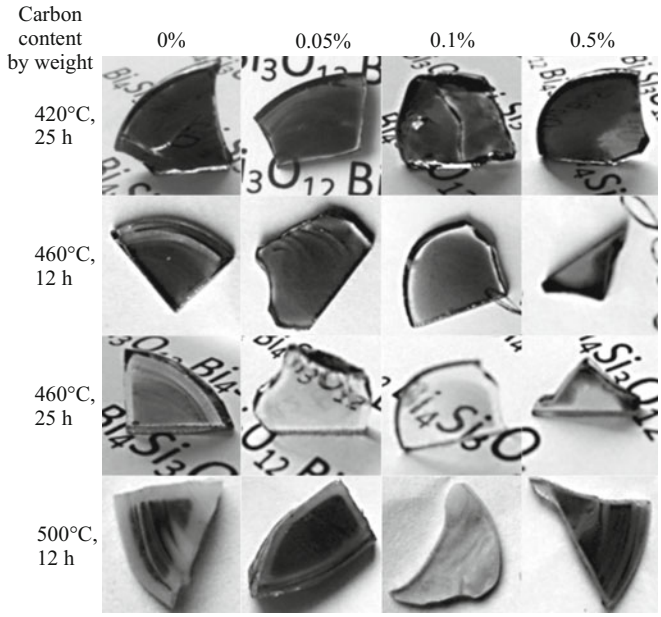

Fig. 3. Heat-treated samples with the composition $Bi_4Si_3O_{12}$.

practically colorless sample with 0.05% carbon shows the lowest absorption (Fig. 3).

The highest absorption is observed in the glass ceramic sample obtained from batch with 0.5% carbon. As noted previously, an increase in the concentration of carbon additives results in the formation of numerous inclusions of a phase of different nature, which is clearly seen under a microscope. This is why the absorption increases in the entire range of wavelengths.

The highest degree of crystallization with loss of transparency is observed in all samples heat-treated at 500°C for 12 h. It is evident visually that the addition of a reducing component conduced to a color change in the glass ceramic samples. After heat treatment for 25 h at 460°C the samples of GCM based on batch containing 0.05 and 0.1% of such an additive were practically colorless with no loss of transparency. This also agrees with the absorption spectra of the samples.

The absorption spectra were obtained with a UNICO 2800 (UV/VIS) spectrophotometer with zone of variation 190 – 1100 nm for the following samples:

– glass with the composition $Bi_4(Si_xGe_{1-x})_3O_{12}$ with x = 0.33, 0.5 and 0.66 after the passage of dc current through them during heating to 500°C;

– glass with the composition $Bi_4(Si_xGe_{1-x})_3O_{12}$ with x = 1, based on batches containing different amounts of carbon, and glass ceramic materials obtained by heat-treating glass at 460°C for 25 h.

The absorption spectra of glass with the composition $Bi_4(Si_xGe_{1-x})_3O_{12}$ with x = 0.33, 0.5 and 0.66 before and after passage of current are presented in Figs. 4 and 5.

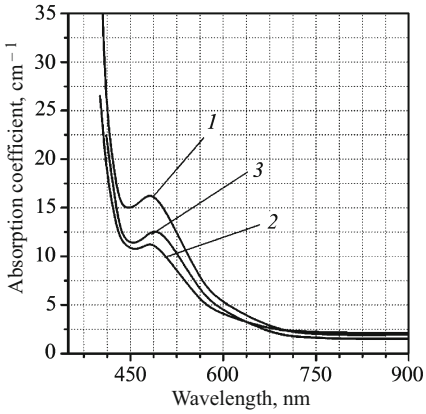

Fig. 4. Absorption spectra of samples of glass with the composition $Bi_4(Si_xGe_{1-x})_3O_{12}$: *1*) $x = 0.33$, *2*) $x = 0.5$, and *3*) $x = 0.66$.

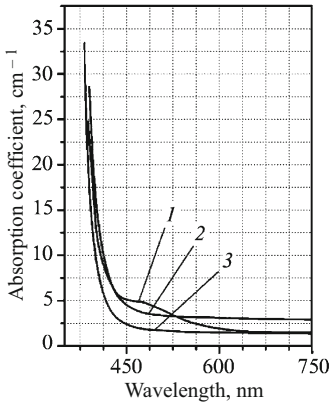

Fig. 5. Absorption spectra of samples of glass with the composition $Bi_4(Si_xGe_{1-x})_3O_{12}$: *1*) $x = 0.33$, *2*) $x = 0.5$, and *3*) $x = 0.66$.

When dc electric current is passed through the samples the indicated absorption peak in the region 450 – 500 nm vanishes.

Probably, in an electric field the oxygen ions, which are the charge carriers in the experimental materials, migrate toward the cathode, which leads to a quantitative increase of the oxygen environment of bismuth, and as a result point defects due to oxygen migration accumulate near the cathode (Fig. 6).

The dark-red layer at the cathode is probably so thin that its presence does not lead to the appearance of appreciable absorption at the wavelength 500 nm.

The absorption spectra obtained for different melting and heat-treatment conditions were compared for a sample with ratio $GeO_2 : SiO_2 = 1 : 2$. The absorption spectra of glasses with the composition $Bi_4(Si_{0.33}Ge_{0.66})_3O_{12}$ are displayed in Fig. 7.

1. The absorption spectrum of a sample of the initial glass with the composition $Bi_4(Si_{0.33}Ge_{0.66})_3O_{12}$. An intense peak is present at 450 – 500 nm. This peak is due to the presence of bismuth ions with oxidation greater than 3+.

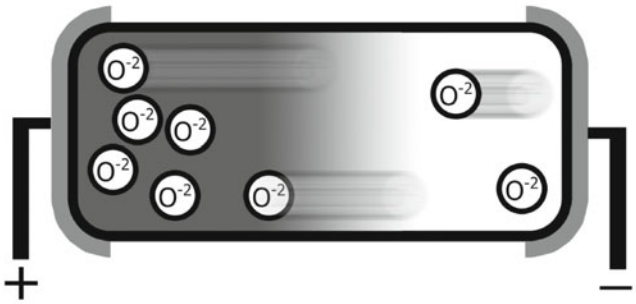

Fig. 6. Diagram illustrating the mechanism of the migration of oxygen ions.

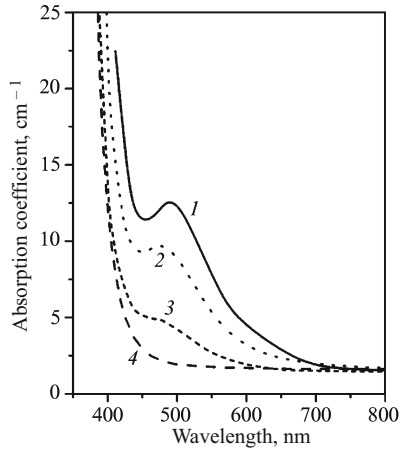

Fig. 7. Absorption spectra of samples of glass with the composition $Bi_4(Si_{0.33}Ge_{0.66})_3O_{12}$: *1*) initial glass, *2*) 500°C, *3*) 500°C + dc current, and *4*) no layer at the cathode.

2. Heating to 500°C during passage of dc current – sharp drop of the peak intensity due to a decrease of the coordination number and valence of bismuth as a result of charge carrier transport.

3. To prove the assertion that the color change is due to the electric current a sample was heated to 500°C with no current. The spectral characteristics remain practically unchanged compared with the initial sample (Fig. 7).

4. The thin dark-red layer containing high-valence bismuth ions was removed mechanically. The peak at 500 nm vanished completely.

The results of the experiment described above suggest that the absorption at the indicated wavelength occurs on bismuth ions with high oxidation (4+, 5+).

The form of the absorption spectrum of $Bi_4Si_3O_{12}$ composition depends on the amount of carbon in the initial batch (Fig. 8).

An absorption band in the region 450 – 500 nm is present in the spectra of all samples.

However, the peak intensity is lowest for the maximum content of carbon in the batch (0.5%). It is logical to attribute this to oxidation-reduction processes occurring in glass in the

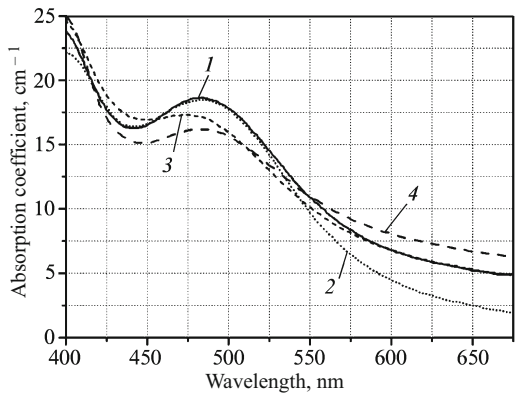

Fig. 8. Absorption spectra of glass with the composition $Bi_4Si_3O_{12}$ with different carbon fraction, %: *1*) 0, *2*) 0.05, *3*) 0.1, and *4*) 0.5.

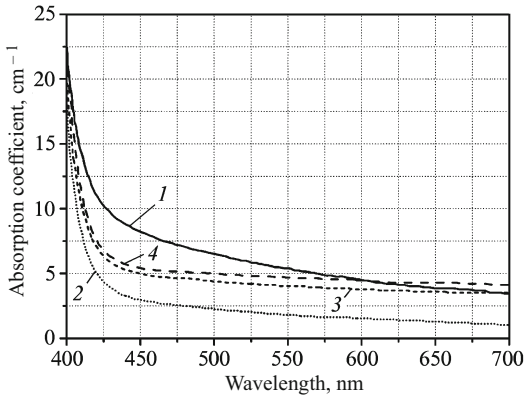

Fig. 9. Absorption spectra of glass ceramic materials (heat-treatment at 460°C for 25 h) with different carbon fraction, %: *1*) 0, *2*) 0.05, *3*) 0.1, and *4*) 0.5.

presence of a reducing component (carbon), if the absorption at the indicated wavelength is due to the presence of bismuth ions with a high degree of oxidation (5+, 4+) while the decrease of absorption is associated with the reduction of bismuth from 5+ to 3+.

The absorption spectra of GCM based on $Bi_4Si_3O_{12}$ glass obtained from batch with different carbon content are displayed in Fig. 9.

As one can see from the plots, the absorption peak at 450 – 500 nm is absent in the absorption spectra of all samples heat-treated at 460°C for 25 h. The intensity of the absorption is different. The transparent and brightest sample with 0.05% carbon possesses the weakest absorption. The sample with 0.5% carbon exhibits the strongest absorption, since an increase of the added carbon concentration results in the formation of inclusions of a phase of different nature which are clearly visible under a microscope. This phase impedes uniform crystallization and leads to nonuniform coloration. This is probably responsible for the increase in the absorption in the entire wavelength range in samples with carbon content above 0.05%.

The following conclusions can be drawn from the results of this work:

– the passage of dc current through the samples of bismuth-containing glasses results in the appearance of narrow dark (near the cathode) and practically colorless regions which are separated by a sharp boundary; this is due to the fact that in an electric field the oxygen ions, which are the charge carriers, migrate toward the cathode, enlarging the oxygen environment of bismuth;

– the glasses obtained from the initial batch with added carbon by melting in air are on the whole transparent; for the lowest carbon contents 0.05 and 0.1% the color of the glasses becomes brighter, since the presence of a reducing component (carbon) in the batch impedes the transition of the initial Bi^{3+} to a higher degree of oxidation 4+, 5+; heat-treatment of such glasses makes it possible to obtain absolutely colorless samples of glass ceramic with no absorption band in the range 450 – 500 nm.

The results of these experiments make it possible to assert that the absorption in the range 450 – 500 nm, which is characteristic for bismuth-containing glasses, obtained by melting in air, as well as glass ceramic materials based on them, is due to the presence in them of bismuth ions with oxidation above 3+.

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